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Boron–Nitrogen Main Chain Analogues of Polystyrene: Poly(*B*-aryl)aminoboranes via Catalytic Dehydrocoupling-v0.95

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Abstract: The first high molar mass polyaminoboranes with an organic substituent at boron, namely the *B*-arylated polyaminoboranes $[NH_2–BHPh]_n$ (**2a**) and $[NH_2–BH(p\text{-}CF_3C_6H_4)]_n$ (**2b**), have been prepared via catalytic dehydropolymerisation. These materials can be considered as inorganic analogues of polystyrene with a B–N main chain. Their synthesis was achieved from *B*-aryl amine–borane precursors in solution using an $[IrH_2(POCOP)]$ precatalyst.

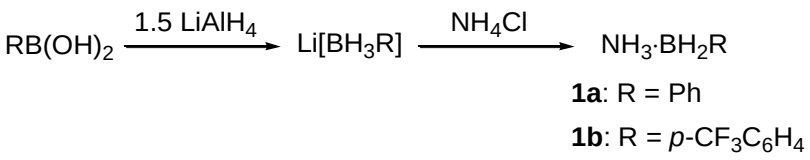
Recent research at the interface of polymer and inorganic chemistry targets the development of hybrid polymers, which combine main group elements with classical organic polymer frameworks leading to novel materials with unique combinations of properties.[1] One strategy to access hybrid polymers involves the formal replacement of C–C units by B–N moieties and has been extensively pursued to create main chain boron-nitrogen analogues of polyolefins[2] and poly(*p*-phenylenes),[3] and more recently unsaturated polymers such as poly(phenylene vinylene),[4] together with a range of other materials.[5] Recently, side chain B-N analogues of polystyrene, namely poly(*B*-vinyl borazines) and poly(*B*-vinyl 1,2-azaborinines) were obtained *via* radical polymerization of the corresponding *B*-substituted monomers.[6] Despite these advances, polystyrene analogues in which the C–C main chain is formally replaced with a B–N skeleton have not been reported to date.

Catalytic dehydrocoupling of amine–boranes, $RR'NH{\cdot}BH_3$ (R = H, alkyl), has attracted considerable attention in recent years due to the potential for applications in hydrogen storage and hydrogen transfer chemistry as well as the potential to access to new inorganic polymeric and BN-containing solid state materials.[7,8] However, to date, only a limited number of amine–boranes, $RNH_2{\cdot}BH_3$ (R = H, Me, Et, *n*Bu), have been dehydropolymerised using transition-metal catalysts to yield soluble polyaminoboranes with *N*-alkyl substituents, $[RNH–BH_2]_n$, isolobal congeners of polyolefins, with potential applications as piezoelectric or preceramic materials.[2,9] The attempted dehydropolymerisation of primary *N*-aryl amine–boranes, $RNH_2{\cdot}BH_3$ (R = Ph, *p*-$MeOC_6H_4$, *p*-$CF_3C_6H_4$), to yield polyaminoborane analogues of polystyrene was prevented by their complex dehydrogenation chemistry in the presence or absence of catalysts that leads to a myriad of products within which no high molar mass polymer was detected.[10]

In contrast to the case of (*N*-organo)amine–boranes, the dehydrocoupling behaviour of their *B*-organo analogues is relatively unexplored.[11,12] We recently reported studies of the catalytic dehydrocoupling

of sterically unhindered *B*-methylated amine–boranes, $RNH_2{\cdot}BH_2Me$ (R = H, Me), using stoichiometric amounts of skeletal nickel.[11b] Although ^{11}B NMR peaks were tentatively assigned to oligomeric or polymeric *B*-methyl aminoboranes, $[RNH–BHMe]_n$ (R = H or Me), under the reaction conditions these intermediates readily underwent further dehydrogenation to yield mainly the *B*-methylated borazines $[RN{-}BMe]_3$ (R = H, Me). We attributed the lability of the $[RNH–BHMe]_n$ oligomers / polymers to the inclusion of an electron-donating methyl group at boron,[11b] which lowers the dissociation energy of the B–N dative bond and thermodynamically facilitates hydrogen elimination, which has been predicted theoretically.[13] We therefore envisaged that replacement of the methyl groups at boron by electron-withdrawing aryl groups should increase the strength of the B–N bonds in the main chain and also their overall stability. Herein, we present our studies of the catalytic dehydropolymerisation of the *B*-aryl amine–boranes $NH_3{\cdot}BH_2Ph$ (**1a**) and $NH_3{\cdot}BH_2(p\text{-}CF_3C_6H_4)$ (**1b**) to give poly(*B*-aryl)aminoboranes, $[NH_2–BHR]_n$ (**2a**: R = Ph, **2b**: R = p-$CF_3C_6H_4$), which are the first examples of inorganic analogues of polystyrene containing a main-chain of alternating B–N groups.

The *B*-aryl amine–boranes **1a** and **1b** were synthesised via the dehydrogenative salt metathesis of $Li[BH_3R]$ and NH_4Cl in an Et_2O/toluene mixture (Scheme 1).[11b,12,14] The lithium trihydridoborate precursor was generated *in situ* via treatment of commercially available $RB(OH)_2$ with 1.5 equivalents of $LiAlH_4$. This protocol afforded amine–(aryl)borane **1a** in 39 % yield as a colourless oil at 25°C, which solidifies upon cooling to −40 °C, and analogue **1b** in 69 % yield as a colourless solid at ambient temperature. The NMR data acquired for **1a** (in $CDCl_3$) and **1b** (in THF-d_8) was consistent with the expected data for *B*-aryl amine–boranes containing four-coordinated boron centres with two hydrogen atoms. For example, the ^{11}B NMR spectra each displayed a single peak at −13.9 (for **1a**) and −11.2 (for **1b**) ppm which appeared as triplets in the ^1H coupled spectra [$^1J_{BH}$ = 95 Hz (**1a**), 96 Hz (**1b**)].



Scheme 1. Synthesis of *B*-arylated amine–boranes **1a** (R = Ph) and **1b** (R = p-$CF_3C_6H_4$).

In line with a higher energy required for dissociation of the B–N bond in **1b** compared to **1a** due to the presence of an electron-withdrawing p-CF_3 group, amine–borane **1b** is stable in the solid state at 20 °C for 170 h, whereas **1a** partially decomposes to give oligomeric $[NH_2–BHPh]_n$ (ca. 20 %) and $NH_3{\cdot}BH_3$ (ca. 5 %) by ^{11}B NMR spectroscopy. Interestingly, both **1a** and **1b** are stable in THF solution at 20 °C for 170 h, providing evidence for the importance of intermolecular reactions in the decomposition pathways of **1a**. Heating of solid **1a** or **1b** or their solutions in THF to 70 °C for 170 h led to full

conversion to an array of products consisting mainly of the borazine [HN-BR]$_3$, but also small quantities of the aminoborane $H_2N{=}BPh_2$ as well as the amine–boranes $NH_3{\cdot}BHPh_2$ and $NH_3{\cdot}BH_3$ were detected by ^{11}B NMR spectroscopy in case of **1a**. These minor products arise from an apparent redistribution of hydrogen and aryl substituents at boron, as found previously for *B*-methyl amine–borane, $NH_3{\cdot}BH_2Me$, on thermal treatment.[11b] The molecular structures of the borazines [HN-BR]$_3$ (R = Ph, *p*-$CF_3C_6H_4$) were also determined by single crystal X-ray diffraction analysis (Figure 1).

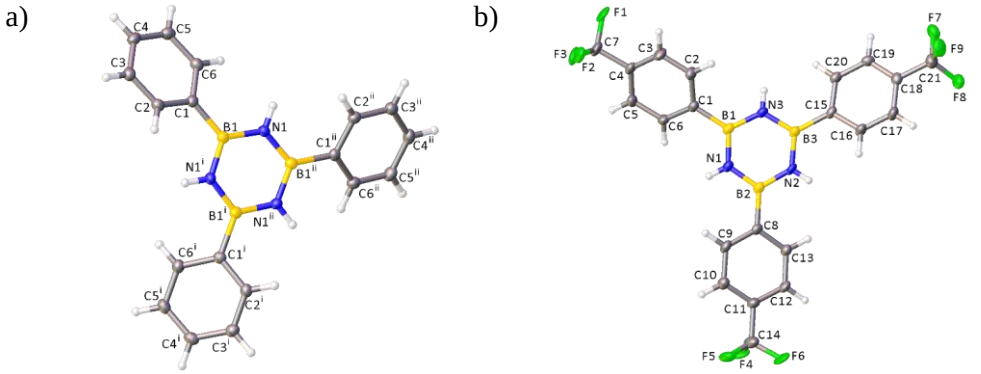
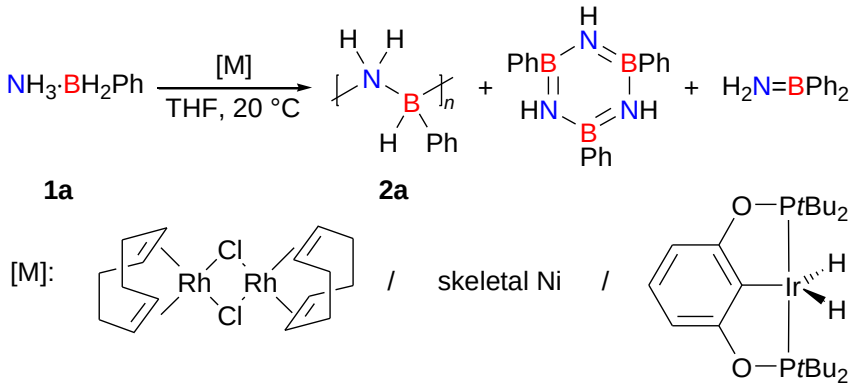


Figure 1. Molecular structures of the borazines [HN-BPh]$_3$ (a) and [HN-B(*p*-$CF_3C_6H_4$)]$_3$ in the solid state.

With the aim of preparing high molecular weight poly(*B*-aryl)aminoboranes, we investigated the dehydropolymerisation of **1a** using [{Rh(COD)(μ-Cl)}$_2$] (COD = 1,5-cyclooctadiene), skeletal nickel and [IrH_2(POCOP)] (POCOP = κ^3-1,3-(*t*$Bu_2PO)_2C_6H_3$), which have previously been reported to be active precatalysts for the dehydrocoupling of amine–boranes (Scheme 2 and Table 1).[2,9e,15] Reaction of **1a** with 2.5 mol % [{Rh(COD)(μ-Cl)}$_2$] (5 % Rh) in THF at 20 °C resulted in the formation of 25 % of aminoborane, $H_2N{=}BPh_2$, 50 % of borazine, [HN-BPh]$_3$, and 25 % of poly(*B*-phenyl)aminoborane, [NH_2–BHPh]$_n$ (**2a**), as detected by ^{11}B NMR spectroscopy of the reaction mixture after 6 h. A significantly slower reaction was observed for the dehydrocoupling of **1a** using 10 mol % skeletal nickel in THF at 20 °C, with only 50 % consumption of **1a** after 70 h to yield **2a** (30 %) and [HN-BPh]$_3$ (20 %). Increasing the amount of skeletal nickel to 100 mol % resulted in quantitative conversion of **1a** at 20 °C in THF within 70 h, leading to the formation of mainly borazine [HN-BPh]$_3$ (70 %) and smaller amounts of **2a** (20 %) and $H_2N{=}BPh_2$ (10 %). The best results were obtained for the dehydrocoupling of **1a** using 5 mol % [IrH_2(POCOP)] in THF at 20 °C, which according to ^{11}B NMR spectroscopy resulted in complete consumption of **1a** to yield the highest proportion of **2a** (75 %), alongside [HN-BPh]$_3$ (25 %) within 1 h.



Scheme 2. Catalytic dehydrocoupling of **1a** with different catalysts [M].

Table 1: Product distribution from the catalytic dehydrocoupling of **1a** in THF at 20 °C ([Rh] = [{Rh(COD)(μ-Cl)}$_2$], [Ir] = [IrH$_2$(POCOP)], [Ni] = skeletal nickel).[a]

Conditions	Time [h]	Conversion of **1a** [%]	Yield of **2a** [%]	[HN-BPh]$_3$ [%]	$H_2N{=}BPh_2$ [%]
2.5 mol % [Rh]	6	100	25	50	25
10 mol % [Ni]	70	50	30	20	0
100 mol % [Ni]	70	100	20	70	10
5 mol % [Ir]	1	100	75	25	0

[a] determined by integration of the signals in the ^{11}B NMR spectra of the reaction mixtures.

In order to further optimise the dehydropolymerisation of **1a** and isolate polymer **2a**, the loading of precatalyst [IrH$_2$(POCOP)] and the reaction time was varied from 0.5 – 5 mol % and 0.5 – 2 h, respectively. After the specified time, the products were precipitated by transferring the THF solution into precooled (−40 °C), stirred *n*-hexane, which resulted in isolation of a colourless solid. The polymer products were analysed by ^{11}B NMR spectroscopy and gel permeation chromatography (GPC). Full conversion of **1a** was only observed in case of employing 5 mol % [IrH$_2$(POCOP)] and afforded high molar mass polymer **2a** with M_n = 96,000 g mol^{-1} (PDI = 1.25; PDI = polydispersity index).

Polymer **2a** of similar molar mass was prepared on a larger scale by dehydropolymerisation of **1a** for 1 h in THF using 5 mol % [IrH_2(POCOP)]. This afforded **2a** as an off-white solid in 34 % yield. Using the same protocol, polymer **2b** was isolated by dehydropolymerisation of **1b** as an off-white solid in 41 % yield. GPC analysis of both solids as solutions in THF (2 mg mL^{-1}) revealed unimodal, molecular weight distributions of modest dispersity and indicated the presence of high molecular weight polymers (**2a**: M_n = 81,600 g mol^{-1}, PDI = 1.33; **2b**: M_n = 86,800 g mol^{-1}, PDI = 1.36; Figure 2). Analysis of the GPC data for **2a** and **2b** in the concentration range of 0.5 – 2 mg mL^{-1} revealed that polymer **2a** showed similar retention volumes within experimental error. In contrast, the fluorinated polymer **2b** displayed a clear inverse dependency of the retention volume on the concentration (see ESI, section 6.3). Thus, polymer **2a** shows the same behaviour in the GPC as observed for *N*-alkyl polyaminoboranes,[9g] whereas the behaviour of fluorinated **2b** in the GPC is reminiscent to that of polyelectrolytes, for which lower concentrations lead to larger interchain repulsions, thereby increasing the observed hydrodynamic radius.[15] Notably, a similar behaviour was recently found for polyphosphinoboranes bearing fluorinated aryl substituents on phosphorus;[16] although no definitive explanation can be provided at the moment, it is postulated that the presence of electron-withdrawing groups at the aryl substituents enhances an accumulation of partial negative charge in the polymer periphery, which leads to interchain repulsion.[17]

The ^{11}B NMR spectra of the polymers displayed broad signals at −7.4 (**2a**, THF) and –7.8 ppm (**2b**, CD_2Cl_2), which appear in a similar region to that for $[MeNH–BH_2]_n$ (δ_B = −6.7 ppm).[2] The ^{1}H NMR spectra of **2a** and **2b** both show broad signals, which may result from different stereochemical environments due to tacticity of the polymers, although further conclusions are hampered by the severe quadrupolar broadening of the signals. The ESI-MS spectra of **2a** (**2b**) show multiple peaks with a difference of 105 (173) *m*/*z* up to 14 (8) repeat units, which correspond to [NH_2–BHR] subunits. (see ESI, Figures S41 and S47).

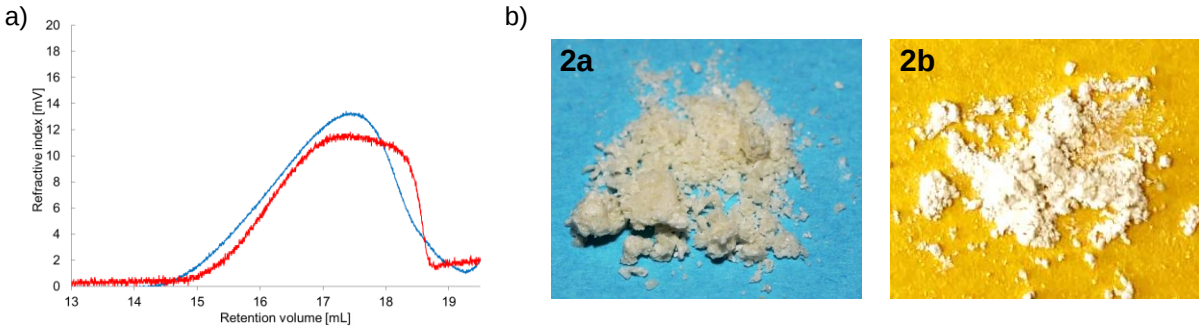


Figure 2. a) GPC chromatograms of **2a** (blue line) and **2b** (red line) in THF (2 mg mL^{-1}) containing 0.1 wt% [nBu$_4$N]Br; b) images of poly(*B*-aryl)aminoboranes **2a** and **2b**.

Polyaminoboranes **2a** and **2b** are stable to the atmosphere and their thermal stabilities were investigated in the solid state as well as in THF solution. This revealed higher stability for the latter material, presumably due to the presence of electron-withdrawing *p*-CF_3 groups in the side chain. For example, polymer **2a** partly decomposes (ca. 40 % conversion) after 170 h at 20 °C in the solid state to give mainly monomeric **1a** and borazine $[HN\text{-}BPh]_3$, whereas polymer **2b** is stable under identical conditions. Thermogravimetric analysis is indicative of thermally-induced dehydrogenation and depolymerisation with low ceramic yields as is often found to linear polymers (for example the char yield of **2a** at 275°C is only 5 %). Branching and crosslinking reactions will need to be introduced to exploit potential utility of these materials as ceramic precursors.

In summary, we report the synthesis and characterisation of the first high molar mass poly(*B*-aryl)aminoboranes **2a** and **2b**, which can be regarded as B–N analogues of polystyrene. Although **2a** was found to be of marginal thermal stability, significant stabilisation was provided by the introduction of an electron withdrawing *para*-CF_3 group on the aryl substituents in **2b**. This offers promise for the future formation of thermally stable materials through the introduction of further electron withdrawing groups on boron. We will also explore the accompanying introduction of electron donating groups on nitrogen which would also be anticipated to lead to materials with increased thermodynamic and kinetic stability, therefore laying the foundation for a full exploration of their properties. We are also exploring the addition of crosslinking additives which should increase ceramic yields and allow an exploration of their utility as precursors to BN/graphitic hybrid materials.

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